

## PATENT ABSTRACTS OF JAPAN

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## (54) PIEZOELECTRIC PORCELAIN COMPOSITION

## (57)Abstract:

PROBLEM TO BE SOLVED: To produce a piezoelectric porcelain composition which contains no lead and has a high mechanical quality factor by using, as constituent atoms or atomic groups of the composition, Bi, Na, TiO<sub>3</sub> and LaFeO<sub>3</sub> in specified compositional ratios, respectively.

SOLUTION: This piezoelectric porcelain composition has a composition represented by the general formula (1-x)(Bi<sub>0.5</sub>Na<sub>0.5</sub>)TiO<sub>3</sub>-xLaFeO<sub>3</sub> (wherein 0<x≤0.3) and is produced by using Bi<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, TiO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, each having high chemical purity, as raw materials of the main constituents. The production process, for example, comprises: blending the above raw materials stoichiometrically with respect to the general formula to obtain a blend; mixing the blend in ethanol for 20 hr; maintaining the mixed material at 800°C for 1 hr to calcine the mixed material; thereafter crushing the calcined material over a 10 hr period; granulating the crushed material with polyvinyl alcohol as a binder into granules; subjecting the granules to press forming under 1 ton/cm<sup>2</sup> pressure into a disklike body having a 20 mm diameter and a 1 mm thickness; sintering the disklike body at 1,100-1,200°C while maintaining the body at that temperature for 2 hr, to form a disklike sintered body; polishing the disklike sintered body so as to form its upper and lower parallel planes to each other; placing two silver electrodes on the upper and lower planes of the sintered body, respectively; and applying a DC electric field having a 4 kV/mm intensity to between the two silver electrodes in silicone oil maintained at 100°C to effect a polarization in the thickness direction in the sintered body. Thus, the objective piezoelectric porcelain composition can be produced and applied to various piezoelectric devices such as filter and vibrator.

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BA10

(54) 【発明の名称】 圧電磁器組成物

(57) 【要約】

【課題】 無鉛で、高い機械的品質係数を有する圧電磁器組成物を提供する。

【解決手段】 一般式  $(1-X)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3 - X\text{LaFeO}_3$  において、 $X$  を  $0 < X \leq 0.3$  の範囲とする。

## 【特許請求の範囲】

【請求項1】 一般式  $(1-X)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3 - X\text{LaFeO}_3$  で表され、 $X$ が  $0 < X \leq 0.3$  の範囲であることを特徴とする圧電磁器組成物。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、波動デバイス、センサー、アクチュエーター等に用いられる圧電磁器組成物に関する。

## 【0002】

【従来の技術】従来、この種の圧電磁器組成物としては、二成分で構成されるPZT ( $\text{PbTiO}_3 - \text{PbZrO}_3$ ) 系磁器や三成分で構成されるPCM [ $\text{PbTiO}_3 - \text{PbZrO}_3 - \text{Pb}(\text{Mg}_{0.5}\text{Nb}_{0.5})\text{TiO}_3$ ] 系磁器が主に用いられてきた。その理由としては、上記の組成物が大きな圧電性を示すことはもちろんであるが、それとともに、その用途がセンサー、アクチュエーター、フィルター等多種にわたり、各用途に要求される特性も様々であるのに対し、上記組成系では、各成分量の割合を調整することにより、要求に対応した特性に適宜に操作できるからである。

【0003】しかし、これらの組成物は、いずれも鉛を主成分とするもので、原料比で酸化鉛として60wt%以上も含まれている。酸化鉛は、低温でも揮発性が高く、仮焼、焼結等の製造時に揮発したり、また、産業廃棄物中から溶出することも考えられる。しかし、これらを予防する対策をするには、設備設置のため膨大な費用を投じなければならない。そこで、無鉛で、大きな圧電特性を示す材料が要望されている。

【0004】また、既存の無鉛圧電磁器組成物、一般式  $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$  は、機械的品質係数の値が低く、高い機械的品質係数が必要とされるフィルター、振動子等の用途に適用させることは困難であった。

## 【0005】

【発明が解決しようとする課題】本発明は、上記の課題を解決し、無鉛で、高い機械的品質係数を有する圧電磁

器組成物を提供することにある。

## 【0006】

【課題を解決するための手段】本発明は、一般式  $(1-X)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3 - X\text{LaFeO}_3$  で表され、 $X$ が  $0 < X \leq 0.3$  の範囲であることを特徴とする圧電磁器組成物である。

## 【0007】

【発明の実施の形態】主成分原料として、化学的に高純度である  $\text{Bi}_2\text{O}_3$ 、 $\text{Na}_2\text{CO}_3$ 、 $\text{TiO}_2$ 、 $\text{La}_2\text{O}_3$ 、 $\text{Fe}_2\text{O}_3$  を用いた。これらを一般式  $(1-X)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3 - X\text{LaFeO}_3$  ( $0 \leq X \leq 0.4$ ) に対し化学量論的に配合し、ボールミルによりエタノール中で20時間混合した。これを800℃で1時間保持して仮焼し、次に、10時間粉砕を行った。バインダーとしてポリビニルアルコールを用い造粒し、圧力1ton/cm<sup>2</sup>で直径20mm、厚さ1mmの円板状に加圧成形した。焼成は、温度1100～1200℃で2時間保持して行った。

【0008】この焼結体を平行平面に研磨し、その上下面に銀電極を設け、100℃のシリコーンオイル中で直流電界4kV/mmを電極間に加え、厚み方向に分極した。

【0009】そして、これらの試料について圧電、誘電特性の測定を行った。圧電特性は、LFインピーダンスアナライザーを用い、共振-反共振法により電気機械結合係数  $k_{33}$ 、 $k_p$ 、 $k_t$ 、機械的品質係数  $Q_m$  を算出し、評価した。また、誘電特性は、LCRメータを用いて周波数1MHzで測定を行い、比誘電率  $\epsilon_{33}^t/\epsilon_0$  で評価した。

【0010】表1に、 $(1-X)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3 - X\text{LaFeO}_3$  において、 $0 \leq X \leq 0.4$  の範囲における  $k_{33}$ 、 $k_p$ 、 $k_t$ 、 $Q_m$  及び  $\epsilon_{33}^t/\epsilon_0$  を示す。なお、 $X=0.4$  の空白は、圧電性が確認できなかったことを示している。また、図1に、 $0 \leq X \leq 0.35$  の範囲の  $k_{33}$ 、 $k_p$ 、 $k_t$  を示す。

## 【0011】

## 【表1】

試料 No.	X	$k_{33}$ (%)	$k_p$ (%)	$k_t$ (%)	$Q_m$	$\epsilon_{33}/\epsilon_0$
1	0	32.3	19.0	37.2	243	285
2	0.05	32.7	21.4	38.2	352	406
3	0.1	34.1	23.4	40.3	413	513
4	0.15	37.2	28.0	41.1	472	602
5	0.2	37.1	26.5	40.5	461	541
6	0.25	36.0	24.1	40.3	432	462
7	0.3	35.6	21.8	38.2	418	395
8	0.35	17.2	9.8	18.3	287	276
9	0.4	-	-	-	-	243

【0012】表1によれば、 $Q_m$ は、 $X=0.15$ で最大値472が得られており、 $(Bi_{0.5}Na_{0.5})TiO_3$ に対し、 $Q_m$ が改善したことがわかる。しかし、 $X=0$ 、 $3<X$ の範囲では、 $Q_m$ が300以下と非常に小さく、実用化は難しいことがわかる。

【0013】また、図1から、 $0<X\leq 0.3$ の範囲では、 $k_{33}$ 、 $k_p$ 、 $k_t$ は、減少していないのに対し、 $3<X$ では、急激に低下している。よって、 $0<X\leq 0.3$ の範囲が実用に適していると考えられる。

【0014】以上より、 $(Bi_{0.5}Na_{0.5})TiO_3$ に $LaFeO_3$ を30mol%まで固溶させることにより、 $(Bi_{0.5}Na_{0.5})TiO_3$ の $k_{33}$ 、 $k_p$ 、 $k_t$ を劣化させることなく、 $Q_m$ を向上させることができ、これにより、フィルター、振動子等の用途へ\*

の適用が可能となる。

【0015】

【発明の効果】以上説明したように、本発明によれば、無鉛で、高い機械的品質係数を有する圧電磁器組成物を提供することができた。

【図面の簡単な説明】

【図1】一般式  $(1-X)(Bi_{0.5}Na_{0.5})TiO_3 - XLaFeO_3$  における  $0\leq X\leq 0.35$  の範囲の  $k_{33}$ 、 $k_p$ 、 $k_t$  を示す図。

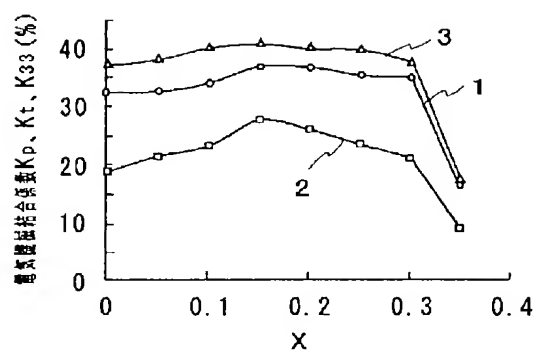
【符号の説明】

1  $k_{33}$

2  $k_p$

3  $k_t$

【図1】



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CLAIMS

[Claim(s)]

[Claim 1] The piezoelectric-ceramics constituent which is expressed with general formula  $(1-X)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{-XLaFeO}_3$ , and is characterized by the range of X being  $0 < X \leq 0.3$ .

[Translation done.]

[Embodiments of the invention] As a principle, the piezoelectric-ceramics constituent was made of  $(1-X)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{-XLaFeO}_3$  (X=0.4) and LaFeO<sub>3</sub>.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the piezoelectric-ceramics constituent used for a wave-motion device, a sensor, an actuator, etc.

[0002]

[Description of the Prior Art] Conventionally, the PCM[PbTiO<sub>3</sub>-PbZrO<sub>3</sub>-Pb(Mg<sub>0.5</sub>Nb<sub>0.5</sub>)TiO<sub>3</sub>] system porcelain which consists of the PZT (PbTiO<sub>3</sub>-PbZrO<sub>3</sub>) system porcelain and three components which consist of two components as this kind of a piezoelectric-ceramics constituent has mainly been used. It is because it can be suitably operated in the property corresponding to the demand when the use covers varieties, such as a sensor, an actuator, and a filter, and adjusts the rate of each amount of components by the above-mentioned composition system to properties required of each use being various with it, although piezoelectric [ as the reason / with the above-mentioned big constituent ] is shown of course.

[0003] However, each of these constituents makes lead a principal component, and is contained more than 60wt% as a lead oxide by the raw material ratio. It volatilizes at the time of manufacture of temporary quenching, sintering, etc., and it is also considered that volatility of a lead oxide is high also at low temperature, and it is eluted out of industrial waste. However, in order to take the measures which prevent these, you have to invest a huge amount of costs for facility installation. Then, the material which shows a piezo-electric unleaded and big property is demanded.

[0004] Moreover, the existing unleaded piezoelectric-ceramics constituent and the general formula (Bi<sub>0.5</sub>Na<sub>0.5</sub>)TiO<sub>3</sub> had the low value of a mechanical quality factor, and it was difficult to have made it apply to the use of the filter for which a high mechanical quality factor is needed, vibrator, etc.

[0005]

[Problem(s) to be Solved by the Invention] this invention solves the above-mentioned technical problem, and is to offer the piezoelectric-ceramics constituent which has a unleaded and high mechanical quality factor.

[0006]

[Means for Solving the Problem] this invention is a piezoelectric-ceramics constituent which is expressed with general formula (1-X) (Bi<sub>0.5</sub>Na<sub>0.5</sub>)TiO<sub>3</sub>-XLaFeO<sub>3</sub>, and is characterized by the range of X being 0 < X ≤ 0.3.

[0007]

[Embodiments of the Invention] As a principal component raw material, Bi<sub>2</sub>O<sub>3</sub> which is a high grade chemically, Na<sub>2</sub>CO<sub>3</sub>, TiO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> were used. These were blended in stoichiometry to general formula (1-X) (Bi<sub>0.5</sub>Na<sub>0.5</sub>)TiO<sub>3</sub>-XLaFeO<sub>3</sub> (0 ≤ X ≤ 0.4), and it mixed in ethanol with the ball mill for 20 hours. At 800 degrees C, this was held for 1 hour, and carried out temporary quenching, next trituration was performed for 10 hours. It corned using polyvinyl alcohol as a binder, and pressing was carried out to disc-like [ with a diameter / of 20mm /, and a thickness of 1mm ] by pressure 1 ton/cm<sup>2</sup>. At the temperature of 1100-1200 degrees C, baking was held for 2 hours and performed.

[0008] This sintered compact was ground at the parallel flat surface, the silver electrode was prepared in the vertical side, 4kV [mm] direct-current electric field were added to inter-electrode in the 100-degree C silicone oil, and it polarized in the thickness direction.

[0009] And measurement of piezo-electricity and dielectric characteristics was performed about these samples. Using LF impedance analyzer, the piezo-electric property computed electromechanical coupling coefficients k<sub>33</sub>, k<sub>p</sub>, and k<sub>t</sub> and the mechanical quality factor Q<sub>m</sub> by the resonance-antiresonating method, and was evaluated. Moreover, dielectric characteristics measured on the frequency of 1MHz using the LCR meter, and specific-inductive-capacity epsilon<sub>33</sub> / epsilon<sub>0</sub> estimated them.

[0010] In TiO(Bi(1-X)0.5Na<sub>0.5</sub>)<sub>3</sub>-XLaFeO<sub>3</sub>, k<sub>33</sub>, k<sub>p</sub>, k<sub>t</sub> and Q<sub>m</sub> in the range, and epsilon<sub>33</sub> / epsilon<sub>0</sub> of 0 ≤ X ≤ 0.4 are shown in Table 1. In addition, the null of X= 0.4 shows that it has not checked piezoelectric. Moreover, k<sub>33</sub>, k<sub>p</sub>, and k<sub>t</sub> of the range of 0 ≤ X ≤ 0.35 are shown in drawing 1.

[0011]

[Table 1]

試料 No.	X	k <sub>33</sub> (%)	k <sub>p</sub> (%)	k <sub>t</sub> (%)	Q <sub>m</sub>	t <sub>33</sub> <sup>1</sup> /t <sub>33</sub> <sup>0</sup>
1	0	32.3	19.0	37.2	243	285
2	0.05	32.7	21.4	38.2	352	406
3	0.1	34.1	23.4	40.3	413	513
4	0.15	37.2	28.0	41.1	472	602
5	0.2	37.1	26.5	40.5	461	541
6	0.25	36.0	24.1	40.3	432	462
7	0.3	35.6	21.8	38.2	418	395
8	0.35	17.2	9.8	18.3	287	276
9	0.4	-	-	-	-	243

[0012] According to Table 1, it turns out that maximum 472 is obtained by X=0.15 and Q<sub>m</sub> has improved Q<sub>m</sub> to TiO (Bi<sub>0.5</sub>Na<sub>0.5</sub>)<sub>3</sub>. However, in the range of X=0 and 3<X, Q<sub>m</sub> is very as small as 300 or less, and it turns out that utilization is difficult.

[0013] Moreover, by 3<X, it is falling from drawing 1 rapidly to k<sub>33</sub>, k<sub>p</sub>, and k<sub>t</sub> not decreasing in 0<X≤0.3. Therefore, the range of 0<X≤0.3 is considered to be suitable for practical use.

[0014] As mentioned above, without degrading k<sub>33</sub>, k<sub>p</sub>, and k<sub>t</sub> of TiO(Bi<sub>0.5</sub>Na<sub>0.5</sub>)<sub>3</sub> by making LaFeO<sub>3</sub> dissolve to 30-mol% to TiO (Bi<sub>0.5</sub>Na<sub>0.5</sub>)<sub>3</sub>, Q<sub>m</sub> can be raised and this becomes applicable to the use of a filter, vibrator, etc.

[0015]

[Effect of the Invention] As explained above, according to this invention, the piezoelectric-ceramics constituent which has a unleaded and high mechanical quality factor was able to be offered.

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[Translation done.]